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THE GENERALIZED STANDARD ADDITION METHOD: INTERMETALLIC INTERFE--ETC(U)

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The Generalized Standard Addition Method:
Intermetallic Interferences in Anodic Stripping Voltammetry.

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Brief

Interferences caused by intermetallic compound formation during analysis by anodic stripping voltammetry are eliminated using the generalized standard addition method.

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Abstract

↓ A barrier to routine application of anodic stripping voltammetry is the possible formation of intermetallic compounds which can lead to significant errors in the estimated analyte concentrations. As the well known method of standard additions can correct only for matrix effects it is powerless to correct for intermetallic interferences which are not matrix effects. By changing the experimental design, the new Generalized Standard Addition Method (GSAM) can simultaneously characterize and correct for this type of interference as well as matrix effects expected for real samples. The method is tested on the Cu-Zn-Hg system and error estimates are provided for calculated linear response constants and analyte concentrations. ↑

The formation of intermetallic compounds in amalgams is a well known phenomena and numerous examples have been documented (1-11). Much interest has been generated in these compounds due to their tendency to cause interference effects in electrochemical studies in methods such as polarography (12) or Anodic Stripping Voltammetry (ASV) (13-15). Kemula and coworkers were the first to recognize their effect on anodic stripping voltammetry, ASV, (6,7,16). Their presence usually caused a reduction in the height of one metal's dissolution wave and occasionally the production of a new peak. Ficker and Meites (17) and Hovsepian and Shain (9) suggested that compounds, such as Zn_2 , also formed in Hg. Later work by Rogers (11) showed that at most only a small fraction of the amalgamated Zn was in the form of a dimer.

Most of the recent work on intermetallics has focused on the Cu-Zn-Hg system. The interaction of Zn with Cu in mercury has been investigated several times with respect to its behavior in ASV (18-20). These recent investigations have been inspired mainly by the increased use of ASV in trace metal analysis of environmental samples (21-22), for in many cases the most abundant trace metals are copper and zinc and the interference effect can hinder analysis.

Though the formation of Cu-Zn compounds in ASV is agreed upon, there are contrasting reports with regard to their stability. A decrease in the Zn peak in the presence of Cu is the most notable feature. Stromberg, et al. (12) monitored stripping currents as a function of the Cu/Zn ratio and attributed their results to the formation of an insoluble 1:1 Cu-Zn compound having a solubility product of 5×10^{-8} . Stromberg, et al. (23) and Mesyats, et al. (24) monitored stripping currents as a function of pre-electrolysis time and concluded that a slightly soluble 1:1 Cu-Zn compound with solubility

product 1×10^{-6} was present. Other investigations have also concluded that the intermetallic Cu-Zn stoichiometry is 1:1 (25-26). Solubility product values have been reported from 1×10^{-5} (26) to 5×10^{-8} (12) with numerous values spanning this range (27).

In contrast to the often reported depression of the Zn peak, the effect of Cu-Zn intermetallic formation on the Cu peak is very small. This has been attributed to another peak from the oxidation of the intermetallic compound at a potential very close to the potential at which Cu is removed (20).

The wide range of solubility products reported demonstrate that the amalgamated Cu-Zn intermetallic system is not easily studied. In a recent paper Shuman, et al. (20) suggested that not only is there a 1:1 Cu-Zn intermetallic present, but also 1:2 and 1:3 species, and that the 1:3 species is insoluble. Their analysis was based on attempts to fit solubility schemes involving a variety of intermetallic species. What can be concluded from the above is the lack of sound information necessary for correction of the Cu-Zn interference during a chemical analysis.

As an alternative, Copeland, et al. (18) discovered that by addition of Ga the Cu-Zn intermetallic interference of the Zn peak could be suppressed. It had previously been shown that Ga forms a Cu-Ga intermetallic (28-29) and this compound is preferentially formed with respect to the Cu-Zn species. This allows Zn to be analyzed for unambiguously, but has the undesired effect of interfering with Cu.

Our approach to the simultaneous analysis of Cu and Zn with anodic stripping voltammetry, outlined below, involves a mathematical analysis scheme designed not only to correct for interference effects in general, but to use

them to advantage. The methodology involved is applicable to the entire range of problems having to do with interference effects.

The Generalized Standard Addition Method

The standard addition method is a well known method for circumventing the problems associated with matrix effects common to many analytical methods. It assumes a linear response and requires the measurement of the analytical signal before and after one or more standard additions have been made to the sample. The initial concentration is found from a regression of the measured signals, or responses as they will be referred to hereafter, to the known concentration change increments. The intercept of this regression line on the concentration axis corresponds to the initial concentration. In general, the response is given by

$$R_{\ell} = ck_{\ell} = (\Delta c + c_0) k_{\ell} \quad 1)$$

where Δc is the concentration change after any standard addition, c_0 is the initial concentration of the analyte and k_{ℓ} is the linear response constant. The real value of the method of standard additions is that calibration is performed in the sample. Matrix effects that would cause k_{ℓ} to be different from calibration solutions to sample are not a problem.

Equation 1 can only be used under certain conditions. It requires the response to be zeroed, the functional relationship to be linear, and the absence of interferences from other components in the sample.

The applicability of Equation 1 to the analysis of multicomponent systems requires the responses to be fully selective (30). Each response must be a function of only one analyte. However, it is not unusual to find examples where the response function is a function of more than one analyte (the interference effect problem). If the interference effects are linear, the total response can be modelled by extending Equation 1 to include contributions

from each analyte as given by

$$R_{\ell} = \sum_{s=1}^r c_s k_{s\ell} \quad 2)$$

where c_s is the concentration of the s^{th} component and $k_{s\ell}$ is the corresponding response constant. Analogous to the expansion in Equation 1, Equation 2 can be expressed as

$$R_{\ell} = \sum_{s=1}^r \Delta c_s k_{s\ell} + \sum_{s=1}^r c_0 k_s \quad 3)$$

In order to make use of Equation 3 the Generalized Standard Addition Method, GSAM (31,32), was developed. It requires that the number of analytical sensors, p , be greater than or equal to the number of analytes, r . Then, it is necessary to measure each response R_{ℓ} , $\ell = 1, p$ before and after the addition of standards. Each standard must, of course, be added at least once; the total number of additions, n , must be greater than or equal to the number of analytes, r . Each response is allowed to depend on any combination of analytes, the only requirement is that every analyte must perturb at least one response.

The preceding equation can be expressed more succinctly as

$$R = C K \quad 4)$$

where R is an $n \times p$ matrix of p measured responses, C is an $n \times r$ matrix whose rows correspond to the total concentration, $\Delta c + c_0$, of each of the r analytes at that particular standard addition, and K is an $r \times p$ matrix whose columns represent sets of response constants for individual sensors. Note that C is initially unknown, for we do not know the initial concentrations,

and that matrix \underline{K} is also unknown. It may also be pointed out that the absence of a particular interference effect will merely result in a zero value at the corresponding element of \underline{K} .

In order to solve for \underline{K} and the original concentrations Equation 4 must be rewritten. If the volume changes associated with the standard additions are negligible, as is often the case when very small volumes of highly concentrated standards are added to a relatively large sample volume, it is possible to separate \underline{C} as

$$\underline{C} = \Delta \underline{C} + \underline{C}_0 \quad 5)$$

where $\Delta \underline{C}$ is the known matrix of total concentration changes arising from the standard additions and \underline{C}_0 is a matrix with identical rows. Since $\Delta \underline{C}$ is a matrix of effective concentration changes at some place during the multiple standard addition procedure, any substantial change in volume will invalidate the definition of \underline{C}_0 above as concentrations are not additive. Fortunately, this is not a problem since a simple volume correction can be made if standard additions cause volume changes (32). Just as \underline{C} can be separated, \underline{R} can also be separated to give a matrix of \underline{R}_0 with all rows equal to the initial responses and a matrix $\Delta \underline{R}$ of response changes caused by n successive standard additions as,

$$\underline{R} = \Delta \underline{R} + \underline{R}_0 \quad 6)$$

Now, the GSAM solves for \underline{K} beginning with,

$$\Delta \underline{R} = \Delta \underline{C} \underline{K} \quad 7)$$

and then uses \underline{K} to find the initial concentrations from the vector of initial responses via,

$$\underline{\underline{C_0}}^T = \underline{\underline{R_0}}^T \underline{K}^{-1} \quad 8)$$

The experimental designs, the complete derivation of the solution for K and Co, and a treatment of deterministic error bounds can be found in the literature (31,32) and therefore is not presented here. The GSAM is a multivariate generalization of the method of standard additions. Responses are recorded before and after known standard additions are made for each analyte. It is the only method that can correct for matrix effects and interferences. In this study, the GSAM was used to overcome the interference effects caused by the formation of intermetallic compounds during an analysis of Cu and Zn by anodic stripping voltammetry.

Experimental

Apparatus:

The computer controlled potentiostat, ASV rotator, glossy carbon electrode, reference electrode, counter electrode, and cell assembly have been described previously (33). The glossy carbon disk electrode was polished prior to each set of runs with 0.5 μm alumina to provide uniform surface conditions for each run. Electrical contact between the reference electrode and the test solution was made through a bridge of saturated potassium chloride.

The potentiostat and rotator were controlled by a Digital Equipment Corporation PDP-11/05 minicomputer and a custom built general purpose interface (34). Cell potentials could be set with a resolution of 1.22 mV and maximum scan rates of $5000 \text{ mV}\cdot\text{s}^{-1}$ and were available with a resolution of $1.22 \text{ mV}\cdot\text{s}^{-1}$. Rotation rates up to 10,000 rpm could be chosen with a resolution of 2.44 rpm. Voltammograms consisted of 256 data points equally spaced between the initial and final voltages determining the scan.

Reagents:

HCl, HNO₃, and KCl were Ultrex grade, (J.T. Baker Co.); KNO₃, CH₃COONa, and CH₃COOH were Baker Analyzed Reagent grade. Standard copper and zinc solutions were prepared by dissolving ultrapure copper powder and zinc oxide (Alfa Products) in a minimum of nitric acid, followed by dilution with distilled water. The Hg(II) plating solution was prepared by dissolving mercury (Baker Instrumental Grade) in a minimum of HNO₃ and diluting to give 0.01 M Hg(NO₃)₂.

Airco prepurified nitrogen was further purified by passage through a washing bottle containing a vanadium (II) solution and then through a second washing bottle containing supporting electrolyte before being used to purge oxygen from the cell solution. All water for this study was purified by passage through a high capacity demineralizing cartridge (Corning 3508-B) and then distilled in a Corning AG-2 quartz still before collection in preleached linear polyethylene containers. All polyethylene bottles and lab glassware were leached for one week in 6N HNO₃ (Baker Analyzed Reagent) and then with distilled water to insure that contamination of the system was minimized (35-38). The cell and electrodes were stored in 6N HNO₃ between runs. Standard additions were made using an Eppendorf 100 µl pipette with disposable tips.

Procedure:

Plating of the electrode and the background-subtracted linear scan anodic stripping voltammetric runs were all carried out under computer control after the run parameters were selected. The procedure used was essentially the same as described elsewhere (33). A mercury film thickness of 300 nm was selected to insure maximum sensitivity. Film thickness below 200 nm have been shown to give reduced sensitivities to both copper and zinc (33,39).

For this study the initial concentrations of copper and zinc were equal to the change in concentration due to their respective standard additions. Runs were started with initial concentrations of 5.3 ppb Cu and 13.3 ppb Zn. All standard additions of Zn were carried out first and then all standard additions of Cu were performed. This method was chosen for two reasons. When run at the maximum sensitivities, the additional Cu would create peaks larger than the capabilities of the system due to the larger capacitive current at the position of the Cu peak. In addition, the coverage of the response surface for subsequent analysis is maximized when all of one components additions are carried out sequentially. If copper and zinc additions had been added alternately, the response surface coverage would be limited to a narrow zone of points, and information relevant to the 2-dimensional nature of the problem would be difficult to recover.

Computer Programs: Fortran IV computer programs used for the Generalized Standard Addition Method calculation are available from Informetrix, Inc. P. O. Box 25808, Seattle, WA 98125

Results and Discussion

A sample consisting of 13.3 ppb Zn and 5.30 ppb Cu was analyzed first by the simple method of standard additions ignoring interference effects, and then by the GSAM. In each case, four additions of Zn were made, each changing the concentration by 13.3 ppb and seven additions of Cu were made each changing the concentration by 5.30 ppb. The size and number of additions were chosen to minimize the total error in the analysis. The results for the GSAM were calculated three different ways; the TDC-GSAM, with unscaled and scaled data and the IDC-GSAM. For each row of ΔR in equation 7, the TDC-GSAM uses the total response changes from the initial responses. Correspondingly, for ΔC it uses the total effective concentration change for each analyte. The IDC-GSAM uses the respective incremental changes from one step in the multiple standard addition procedure to the next step. Scaling involves making the resulting rows of the ΔR matrix have a vector norm equal to one. This scaling forces every concentration change term in ΔR to the same vector length on the multi-dimensional response surface. Its effect in this case is to remove any bias due to the different magnitudes of the responses.

The final analysis results are shown in Table I. The predicted initial concentrations using the simple method of standard additions is predictably low due to the interference caused by intermetallic formation. The results for the various calculation variations of the GSAM are substantially the same and amount to a considerable improvement over the results obtained using the method of standard additions.

Table II contains the K matrix of linear response constants as calculated using the IDC-GSAM. The results using the other GSAM variations are essentially the same. The individual values show the effect of each metal on each sensor.

The relative size of $k_{Zn,Zn}$ to $k_{Cu,Cu}$ is an indication of the sensitivity of the method to the two analytes. The interference coefficients are both negative as is expected when an intermetallic compound is formed. The small negative value for $k_{Cu,Zn}$ is consistent with the previously mentioned report that the CuZn intermetallic species is oxidized at a potential very near to where Cu is removed.

Using the GSAM, accurate results for the determination of Cu on Zn by ASV can easily be obtained. Our laboratory routinely uses the GSAM as it is simple and provides accurate results.

The interference of Cu on the analysis of Zn can be compensated for but not without paying a price. The theory of multicomponent analysis in the presence of interferences (32) states that when interferences are large, measurement errors actually can be amplified to produce larger uncertainties in the estimates of the response constants and initial analyte concentrations. An upper bound to this error amplification is the condition number of the matrix K . The $\text{cond}(K)$ for K in Table II is 2.68 meaning that, in the worst case, the relative error in measuring the responses can be multiplied by 2.68 to give the relative error in final concentration estimates. However, it should be remembered that this is a worst case upper bound.

When one considers all of the possible sources of error, propagation becomes much more complicated (32). In fact, upper bound relative error estimates given a $\text{cond}(K)$ of 2.68, an estimated 1% error in making standard additions and taking into account response errors and errors in the estimated response constants are 7% for Zn and 13% for Cu.

Because the error bounds are truly only bounds, a further error propagation analysis was undertaken. Ten response matrices were calculated by perturbing the measured response matrix with a random normal error with mean zero and standard derivation equal to the measured errors in the responses. The GSAM calculations were carried out on all sets. The mean and standard deviation of these ten sets of GSAM results were then calculated (Table III) and can be compared to those presented in Tables I and II.

Though the condition of K is large, the resulting relative error in C_0 is less than 2% for zinc and less than 4% for copper. These error values are much more realistic than the mathematical bounds generated previously.

Finally, it should be noted that the true values fit well within the 95% confidence interval about the mean values (Table III) or the calculated values from the GSAM (Table I). Zn at 13.3 ppb is within one standard deviation to the estimated concentration and Cu is within two standard deviations.

Conclusion

The ability to compensate for intermetallic interference effects in anodic stripping voltammetry has been demonstrated. The often reported effect of Cu interfering with Zn can be eliminated and ability to simultaneously monitor Cu has been substantially improved. Three alternate methods of approaching the analysis of the data were used with no results clearly favoring the use of any particular one. Though the conditions associated with any chosen experimental design will favor one variant of GSAM over another, it is presently unclear how an aprior determination of one design over another may be made.

In addition, an error analysis was undertaken. Error bounds found through the application of advanced numerical analysis methods appear to be overly broad. Until further studies are made with improved error estimates, a more reasonable approach is to rely upon the results from the solution of several perturbed data sets. However, this does not diminish the value of the error bound calculation for demonstrating how the overall experimental design may be improved.

The generalized standard addition method should be used for eliminating not only the interference effects of intermetallic compounds in ASV, but interference effects and matrix effects in many other methods, and of other origins (spectral, chemical, physical), as well. Its application depends only upon the ability to obtain the required number of responses while making standard additions.

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Table I

Estimated Initial Concentrations (ppb)

	<u>[Zn].</u>	<u>Analysis error</u>	<u>[Cu].</u>	<u>% error</u>
True	13.30	_____	5.30	_____
Simple Standard Addition	10.37	22.0%	4.82	9.0%
TDC-GSAM	13.38	0.6%	5.02	5.3%
TDC-GSAM (Scaled)	13.41	0.8%	5.02	5.3%
IDC-GSAM	13.17	1.0%	5.01	5.5%

Table II

Linear Response Constants

IDC-GSAM

	<u>Zn peak</u>	<u>Cu peak</u>
Zn	60.55	-0.47
Cu	-13.66	24.06

Table III

Uncertainty Perturbation Results (IDC-GSAM)

(mean values of ten calculations with standard deviations in parentheses)

K matrix

	<u>Zn peak</u>	<u>Cu peak</u>
Zn	60.57 (0.18)	-0.50 (0.19)
Cu	-13.68 (0.10)	24.07 (0.11)

Initial Concentrations (ppb)

[Zn]₀ = 13.15 (0.23)

[Cu]₀ = 5.01 (0.20)

